Process/Equipment Co-Simulation on the Syngas Chemical Looping Process

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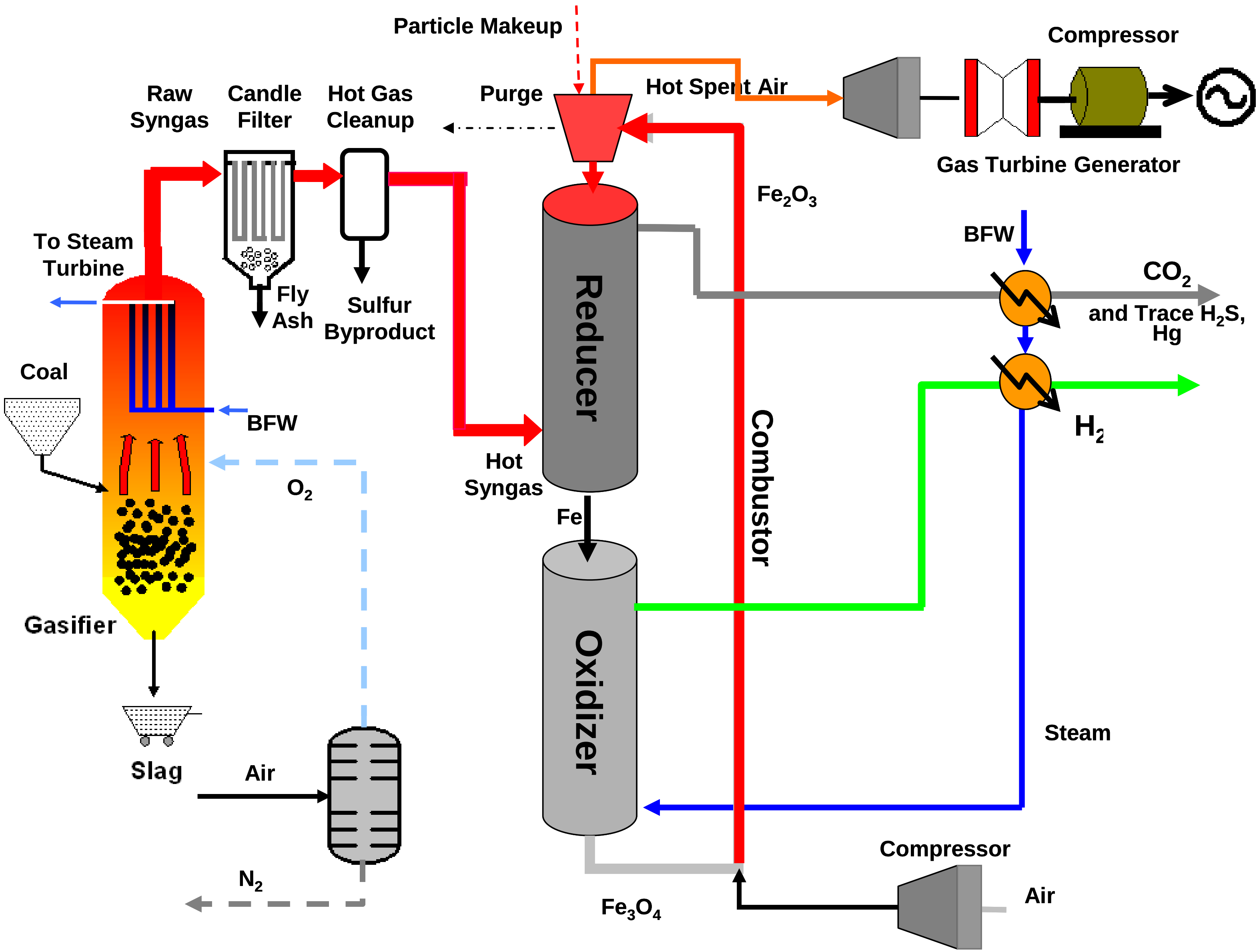
Syngas Chemical Looping Process



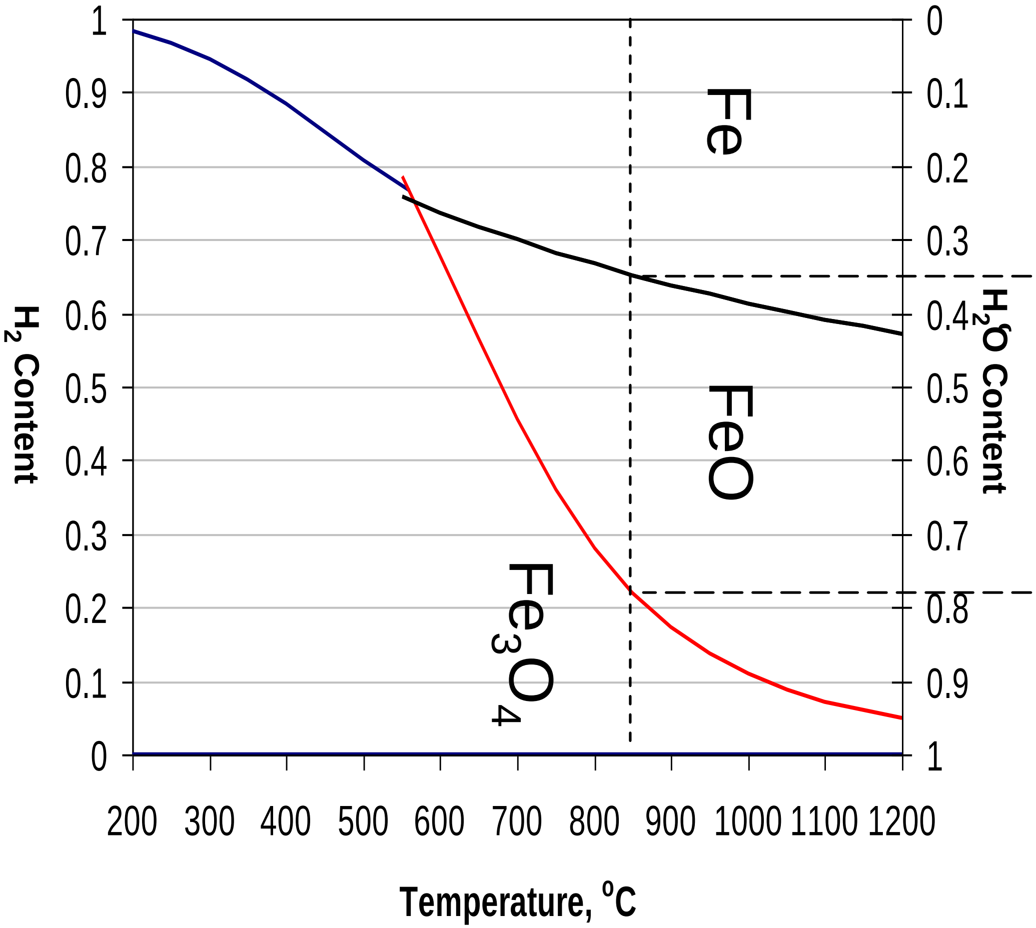
Chemical Looping Reactor System

- Reducer $CO/H_2O+Fe_2O_3 \rightarrow CO_2/H_2O+FeO_x$
- Oxidizer $H_2O+FeO_x \rightarrow H_2+Fe_3O_4$ ($x<1.33$)
- Combustor $Fe_3O_4+O_2 \rightarrow Fe_2O_3$

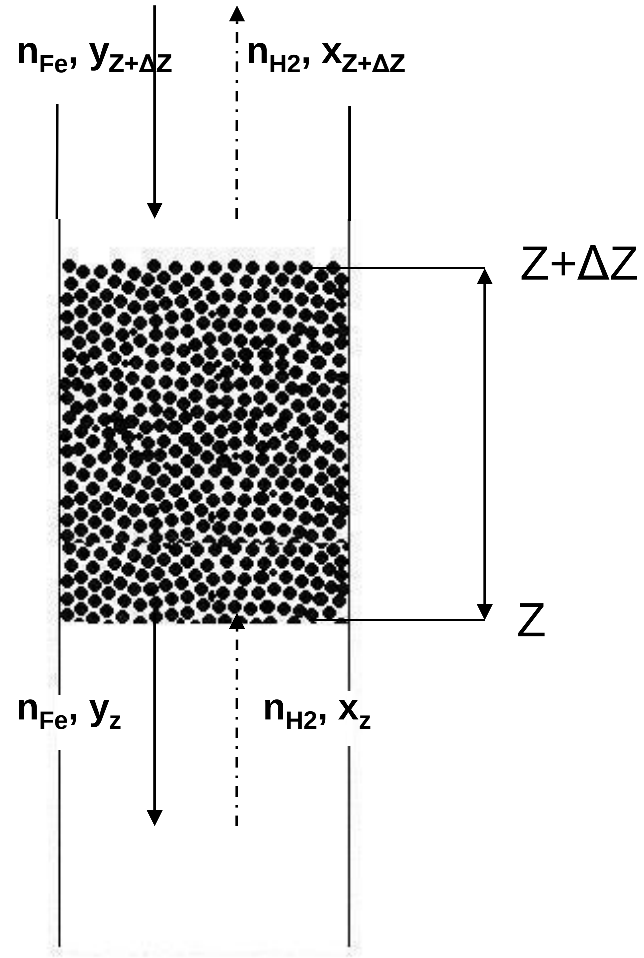
- Reactor Type
  - Fluidized bed reactor design
  - Moving bed reactor design (OSU)

Thermodynamic Analysis on Reducer

Thermodynamic Restrictions for Fluidized Bed Reducer under 850 C



Operating Equation for Moving Bed Reducer



Fixed solid molar flowrate n_{Fe},

Oxygen content for solid $$y = \frac{3n_{Fe_2O_3} + 4n_{Fe_3O_4} + n_{FeO}}{n_{Fe}}$$

Fixed gas molar flowrate $n_{H2} + n_{H2O}$,

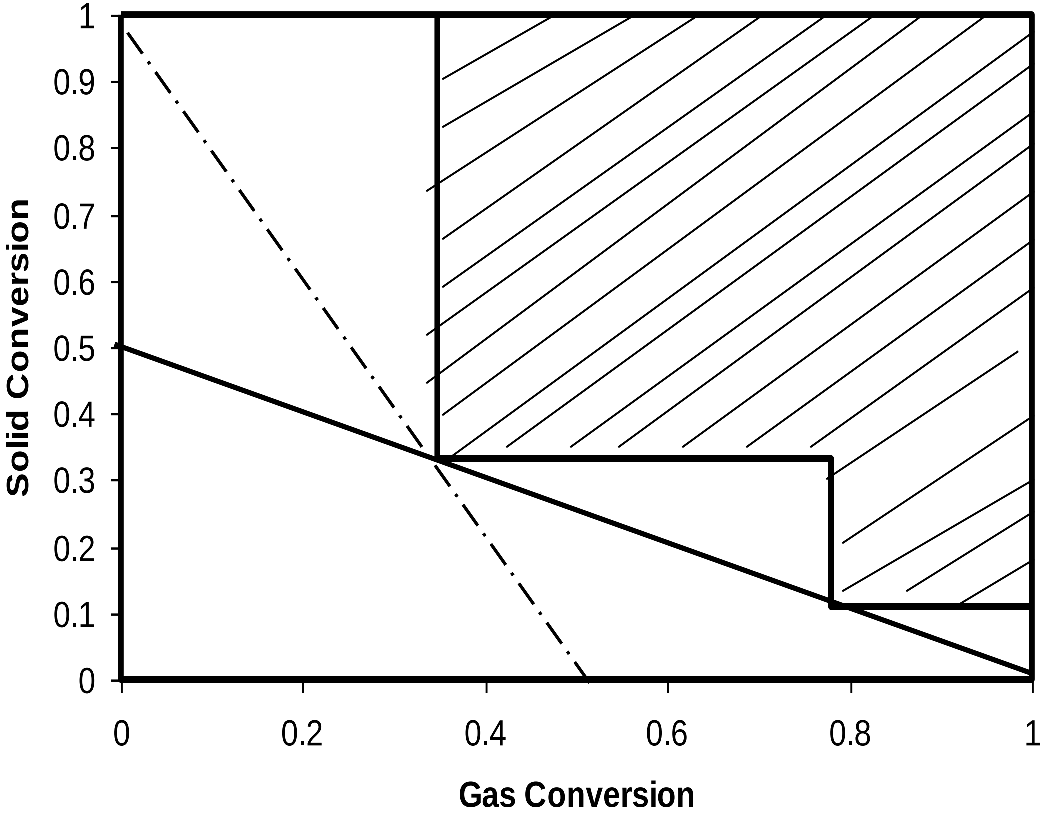
Oxygen content for gas $$x = \frac{n_{H_2O}}{n_{H_2} + n_{H_2O}}$$

Oxygen Balance $$n_{Fe}(y_{z+\Delta z} - y_z) = (n_{H_2} + n_{H_2O})(x_{z+\Delta z} - x_z)$$

$$\Delta z \to 0 \Rightarrow dy/dx = (n_{H_2} + n_{H_2O})/n_{Fe}$$

It is a linear equation when feeding ratio is fixed

Operating Lines in a Countercurrent Moving Bed Reactor under 850ºC



The operating line is straight when feeding ratio is fixed: solid line represents full gas conversion with minimum solid requirements, dash line reaches full solid conversion with minimum gas requirements

Equilibrium Reactor Modeling

ASPEN Plus® Model Setup

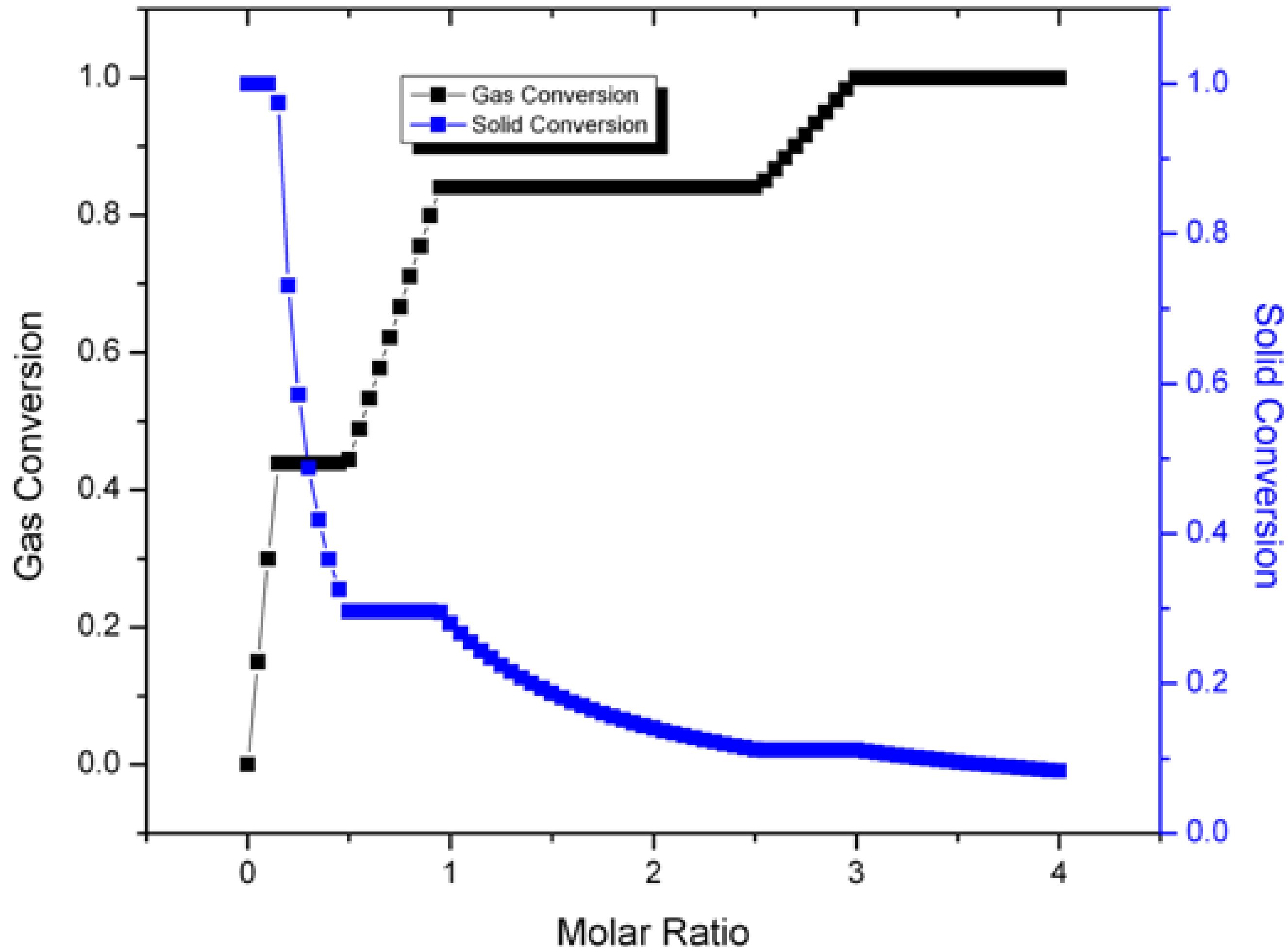
Name of the Parameter	Parameter Setting
Reactor Module	RGIBBS
Physical and Thermodynamic Databanks	COMBUST, INORGANIC, SOLIDS and PURE
Stream Class	MIXCISLD
Property Method (for Gas and Liquid)	PR-BM
Calculation Algorithm	Sequential Modular (SM)

Physical Property Calibration

Components	FE_2O_3	FE_3O_4	FE	$FE_{0.947}O$
Temperature units	˚C	˚C	˚C	˚C
Property units	J/kmol	J/kmol	J/kmol	J/kmol
T1	25	576.8500000	25	25.00000000
T2	686.85	1596.850000	626.85	1376.850000
a	-9.28E+08	-9.7072850E+8	3.78E+07	-2.8212753E+8
a’	-9.28E+08	-9.5672850E+8	3.78E+07	-2.81844E+8
b	1.98E+06	5.27383876E+5	-6.54E+05	4.01635664E+5
b’	1.98E+06	5.355839E+05	-6.54E+05	4.029657E+05
c	-2.58E+05	-50171.18100	1.09E+05	-4.878544E+04
c’	1.98E+06	-5.089700E+04	-6.54E+05	-4.860400E+04
d	165.486384	-35.96733770	-214.129205	-4.184000020
e	-0.066806967	-6.0151695E-5	0.084705631	0.0
f	1.17E-05	6.12900216E-9	-1.95E-05	0.0
g	7.66E+09	-4.277784E+10	-4.01E+09	1.40164001E+8
h	-3.76E+11	5.46763727E+9	1.98E+11	0.0

Revised data is consistent with literature and experiments

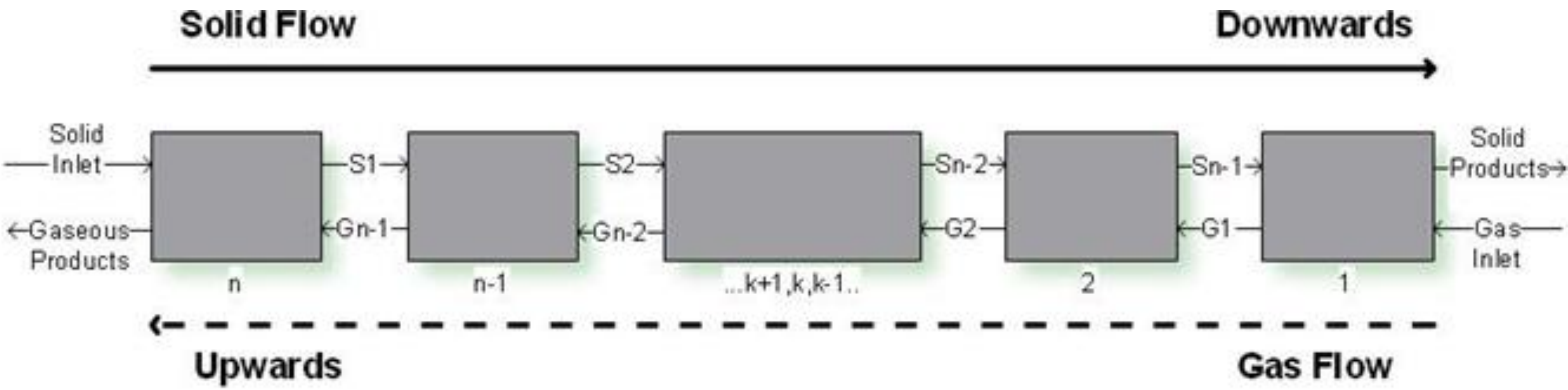
Fluidized Bed Reducer Modeling



RGibbs reactor model, 850 C, 1 atm

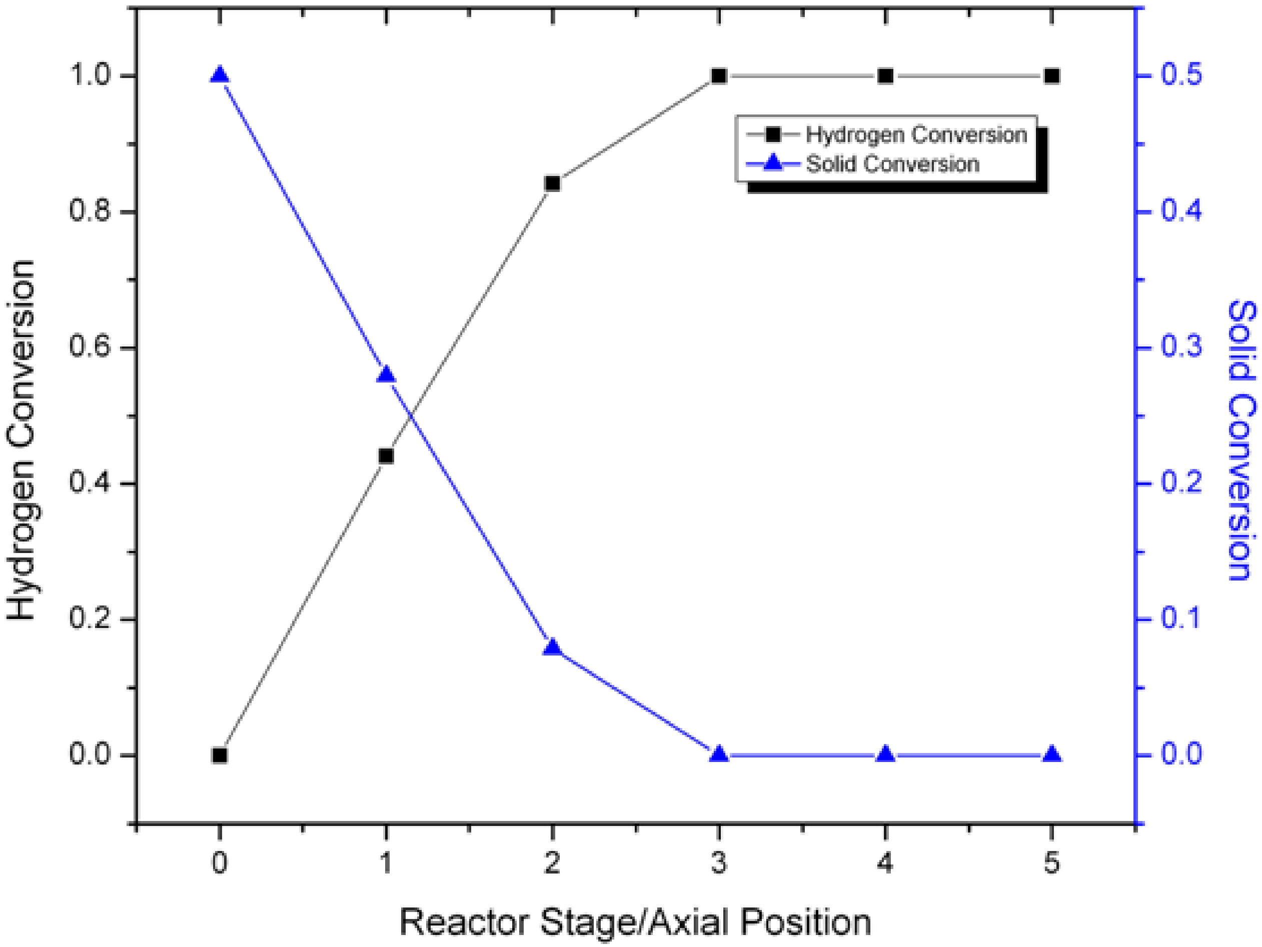
Fluidized bed reducer requires a ratio of >3 to fully convert H_2

Moving Bed Reducer Modeling



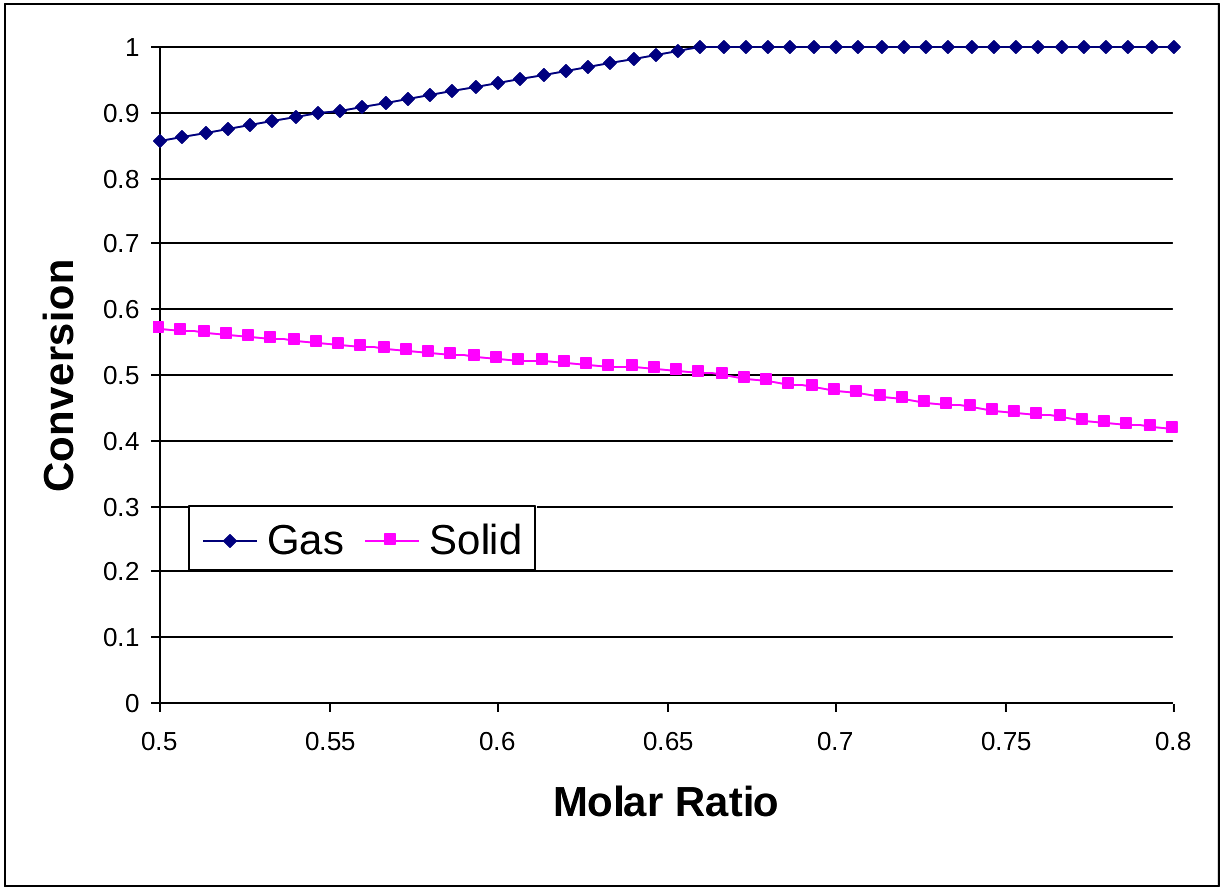
Multistage equilibrium model to mimic the gas solid countercurrent flow

5-stage Equilibrium Moving Bed Reducer



850 C, 1 atm, M_{Fe2O3}:M_{H2}= 2:3

Conversions vs Molar Flow Rate Ratio in the Moving Bed Reducer



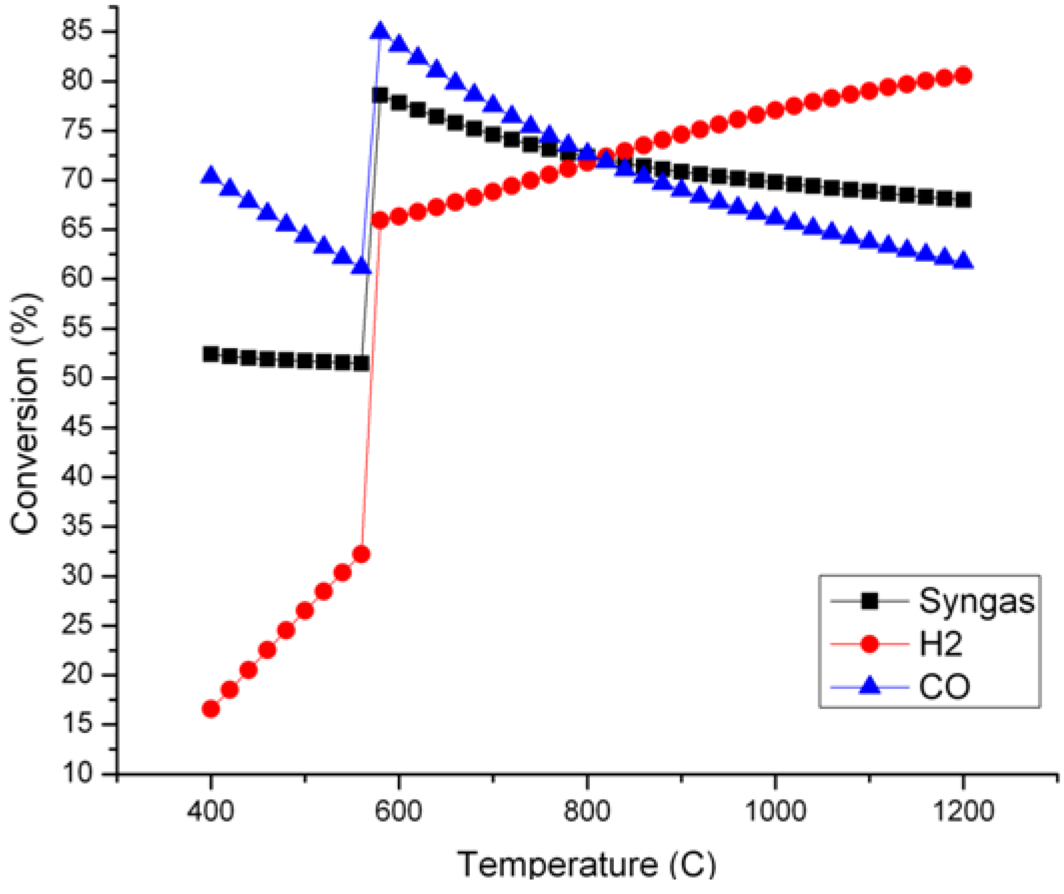
Multistage equilibrium reactor model, 850 C, 1 atm

Moving bed reducer requires a ratio of >0.66 to fully convert H_2

SCL Reducer Modeling

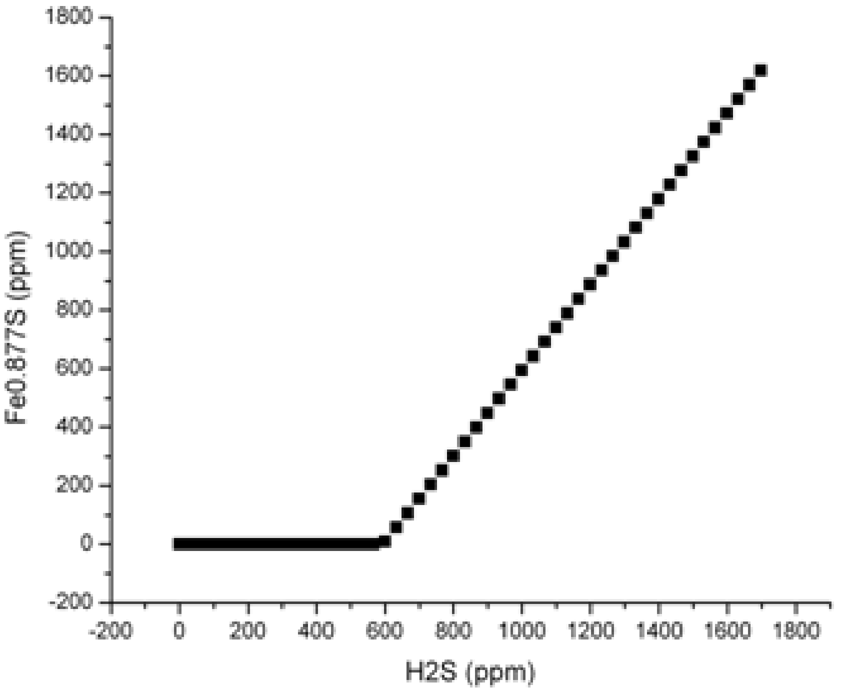
Reactor Type (Reducer)	Fluidized Bed	Moving Bed (OSU)
Gas Solid Contacting Pattern	Well-mixed	Countercurrent
Syngas Conversion	100%	100%
Molar Flowrate Ratio Between Solid and Gas	3:1	2:3
Oxygen Carrier Conversion	11.1% (Fe_3O_4)	49.6% (Fe & FeO)
Subsequent Hydrogen Production	No	Yes

Temperature Effect on Moving Bed Reducer Performance



Multistage equilibrium reactor model, CO:H_2=2:1 syngas input, 1 atm

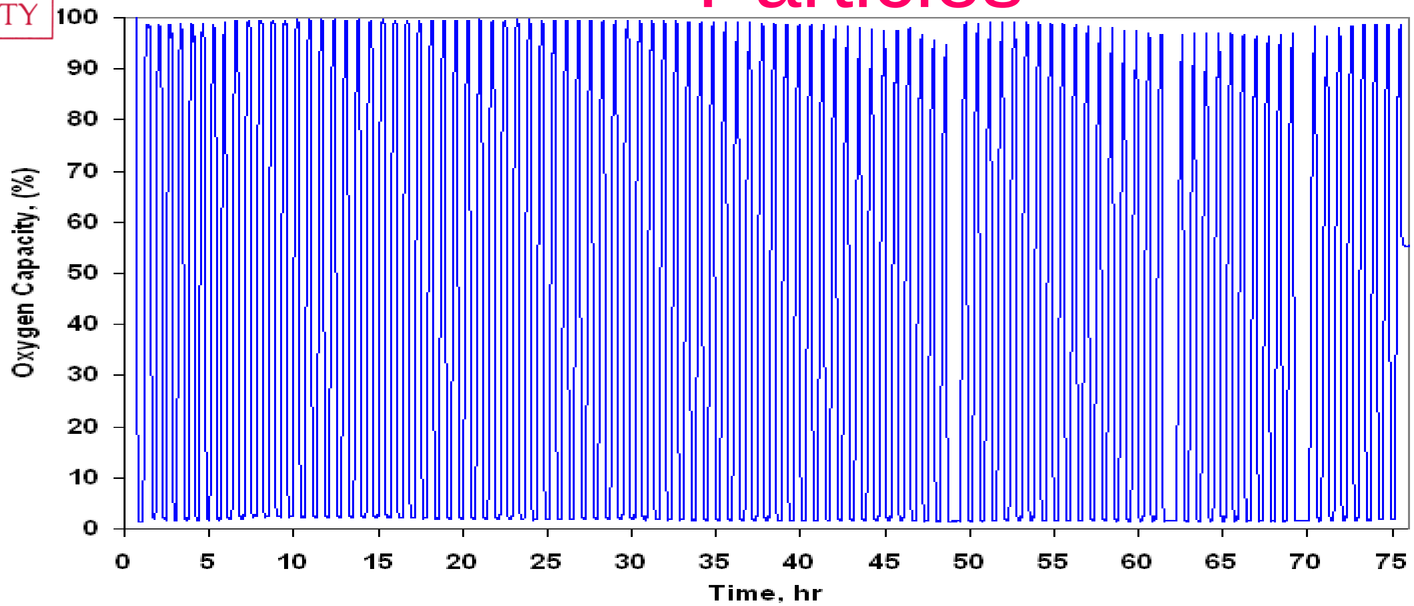
Fates of Sulfur and Mercury

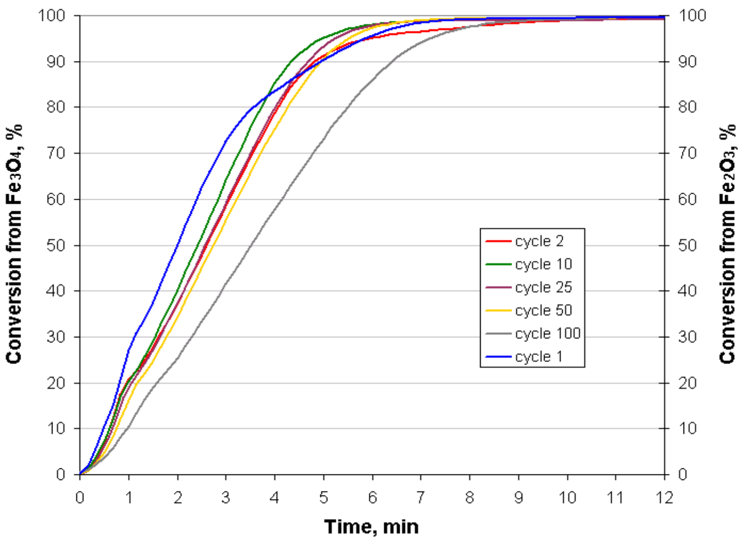


- Sulfur will exit in SO_2 from the top, and start accumulating in solid as $Fe_{0.877}S$ when H_2S>600 ppm
- All the mercury will exit in gas phase

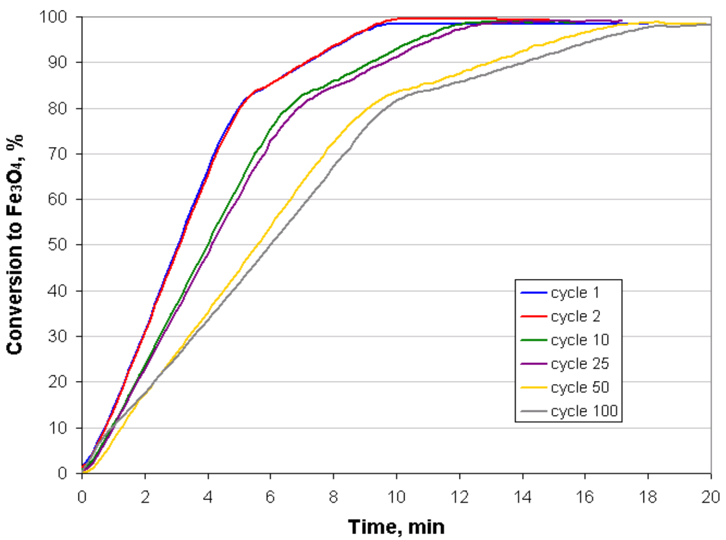
Experimental Study

Recyclability of Composite Fe_2O_3 Particles





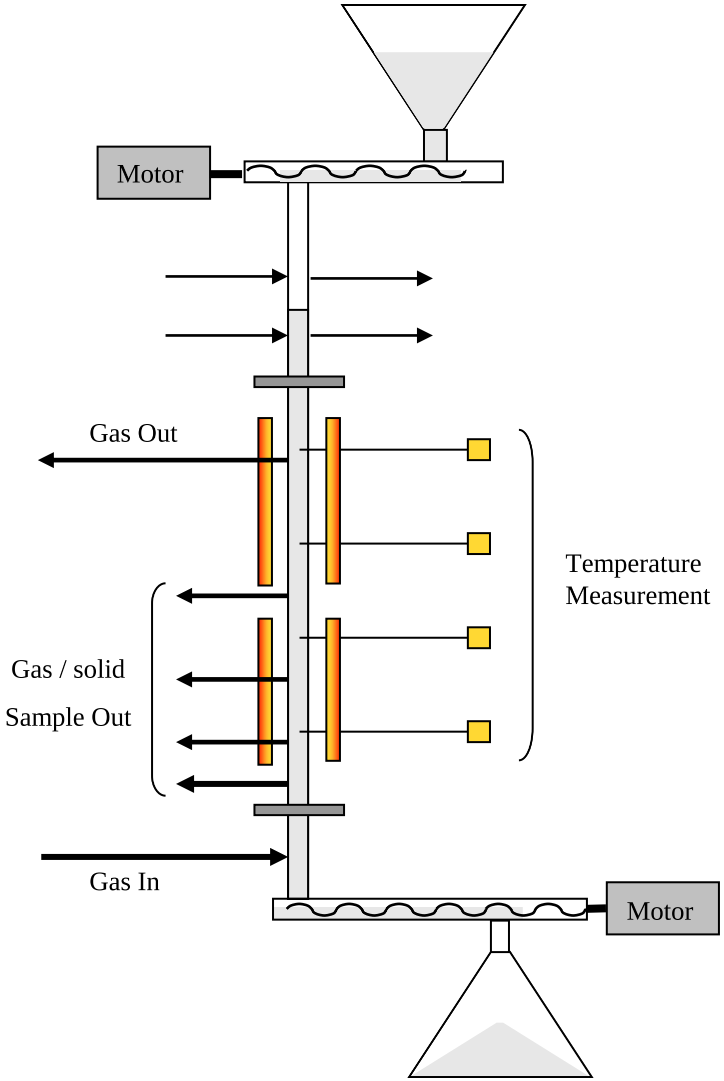
Reduction

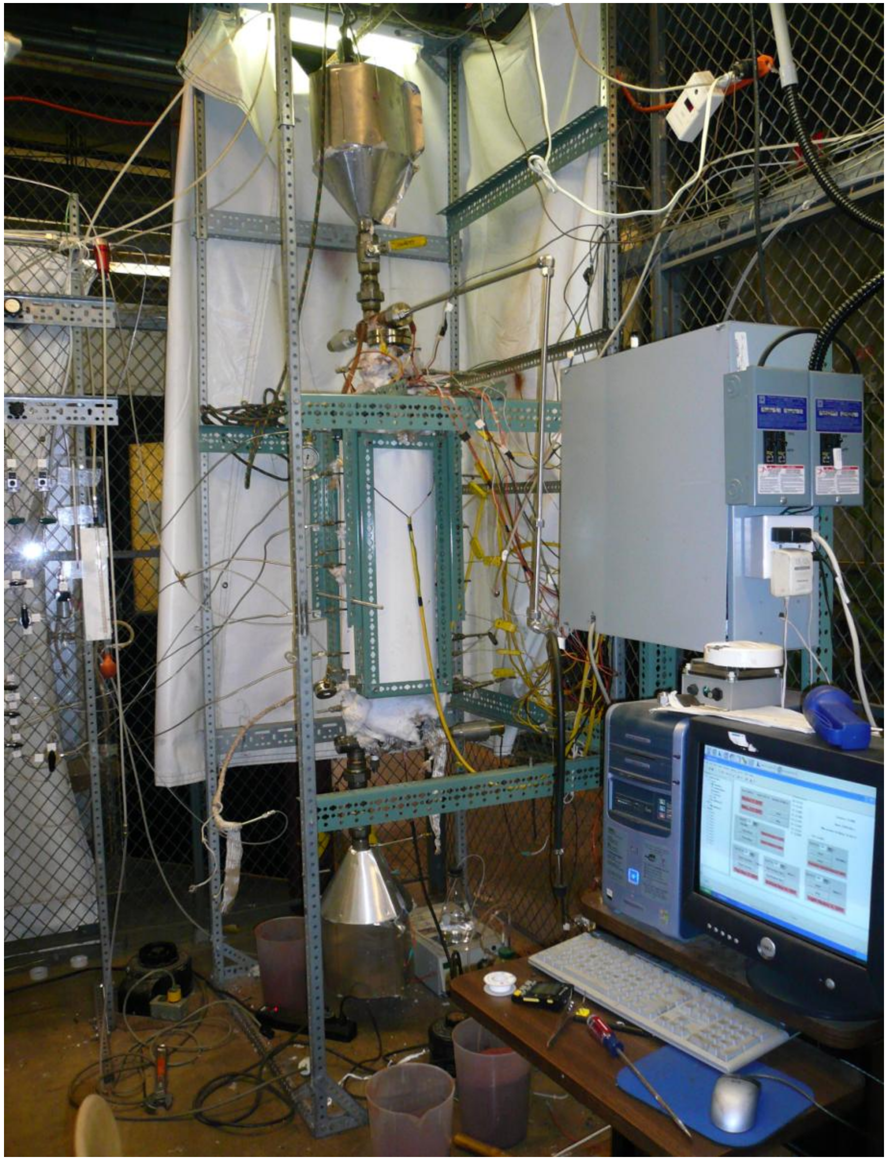


Oxidation

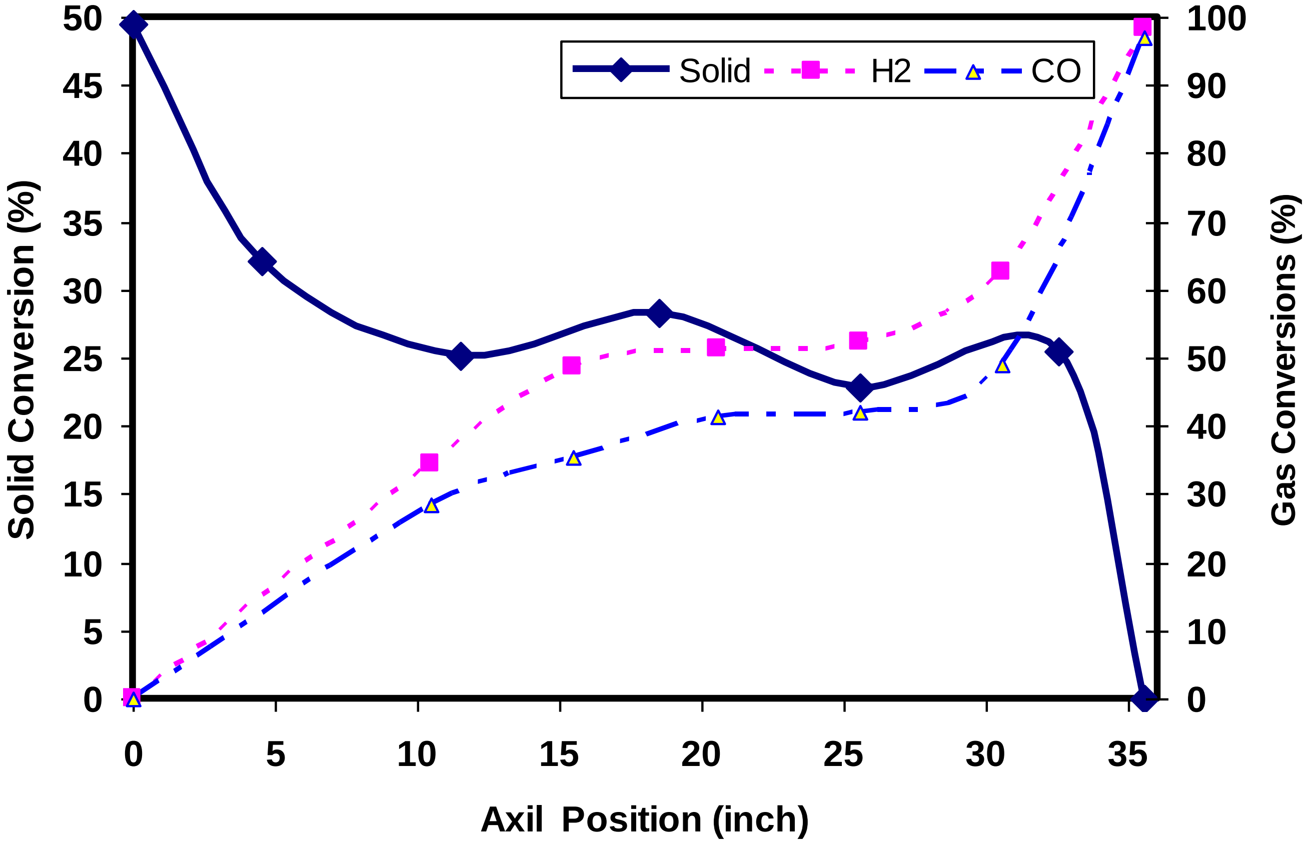
Iron Based Composite particles are completely recyclable for more than 100 cycles

Reducer Modeling Validation



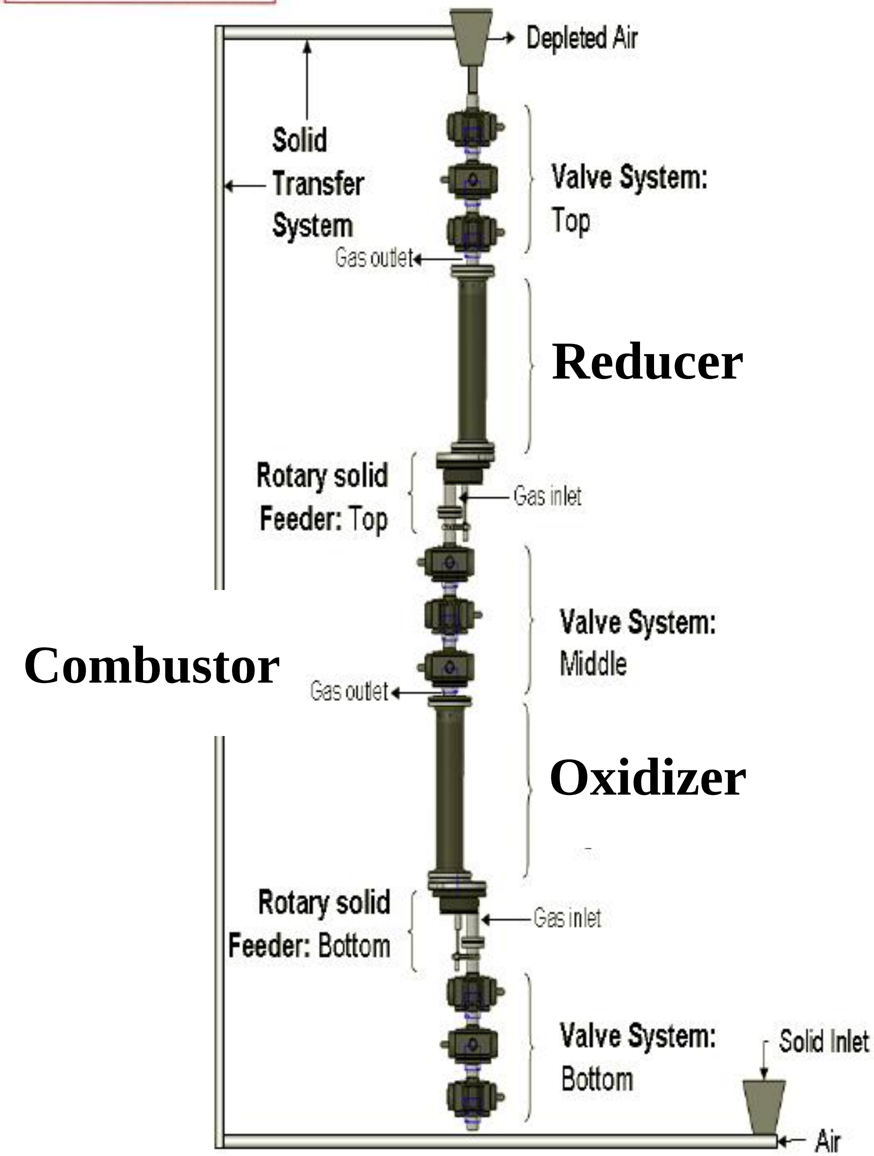


Moving Bed Studies – Reducer Operation



Nearly 100% conversion of syngas achieved

Phase I – Sub Pilot Scale SCL plant



Process Simulation

Common Assumptions

- A 1000 MWt (HHV) Illinois #6 coal input
- Shell Gasifier is considered
- Carbon regulation mandates > 90% carbon captured
- The H_2 coming out of the system is compressed to 30 atm for transportation while the CO_2 is compressed to 150 atm for geological sequestration

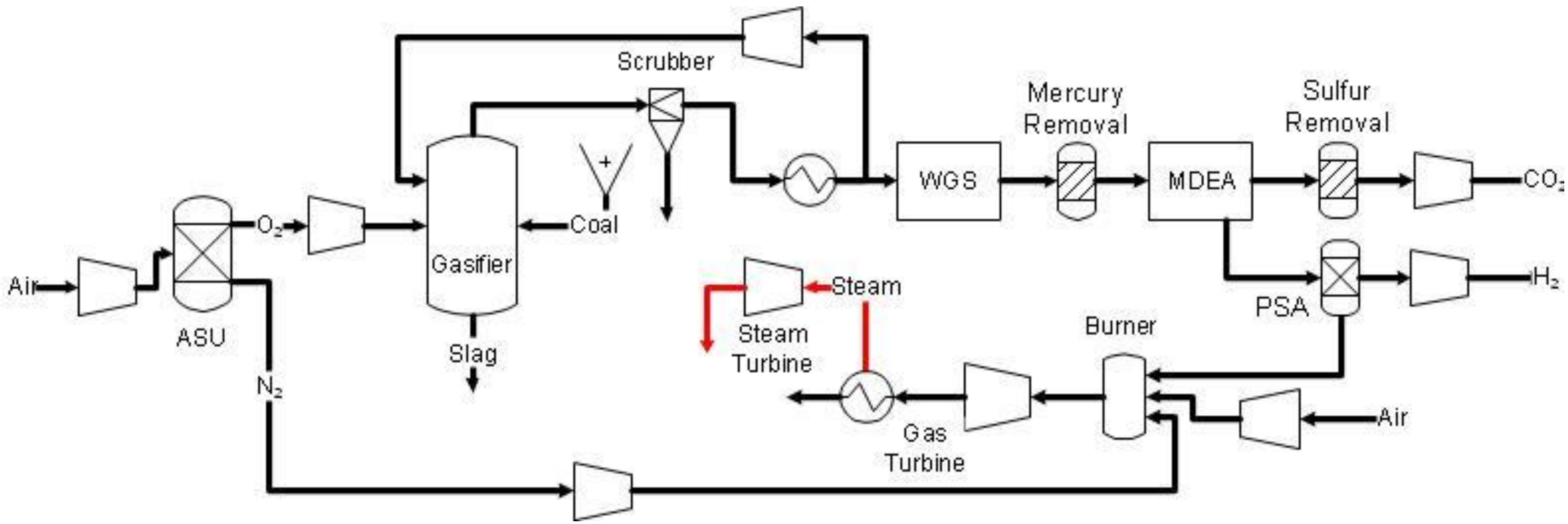
Assumptions used are similar to those adopted by Mitretek Systems in their report to USDOE/NETL*.

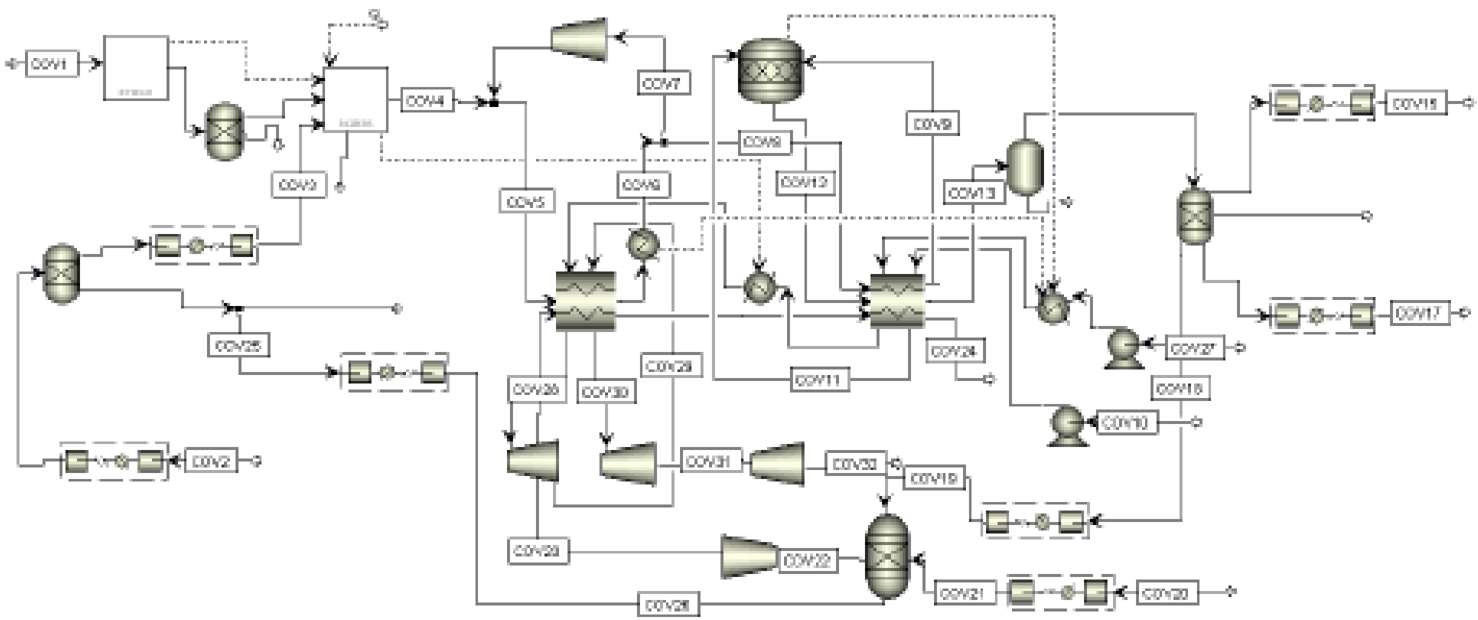
** Gray D. and Tomlinson G. Hydrogen from Coal. Mitretek Technical Paper. DOE contract No:DE-AM26-99FT40465. (2002)*

ASPEN Models for the Key Units

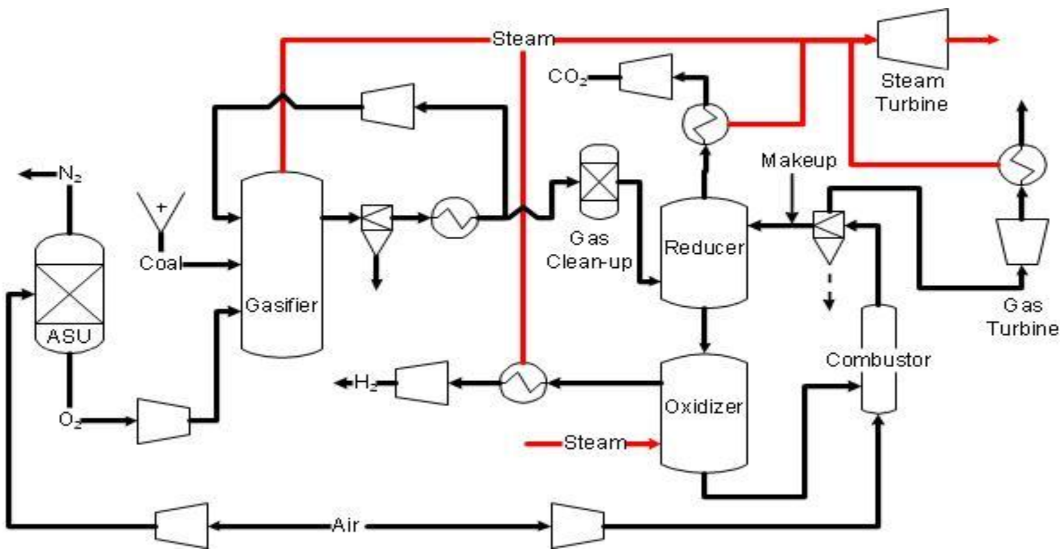
Unit Operation	Aspen Plus® Model	Comments / Specifications
Air Separation Unit	Sep	Energy consumption of the ASU is based on specifications of commercial ASU/compressors load.
Coal Decomposition	Ryield	Virtually decompose coal to various components (Pre-requisite step for gasification modeling)
Coal Gasification	Rgibbs	Thermodynamic modeling of gasification
Quench	Flash2	Phase equilibrium calculation for cooling
WGS	Rstoic or Rgibbs	Simulation of conversion of WGS reaction based on either WGS design specifications or thermodynamics
MDEA	Sep or Radfrac	Simulation of acid gas removal based on design specifications
Burner	Rgibbs or Rstoic	Modeling of H_2/syngas combustion step
HRSG	MHeatX	Modeling of heat exchanging among multiple streams
Gas Compressors	Compr or Mcompr	Evaluation of power consumption for gas compression
Heater and Cooler	Heater	Simulation of heat exchange for syngas cooling and preheating
Turbine	Compr	Calculation of power produced from gas turbine and steam turbine

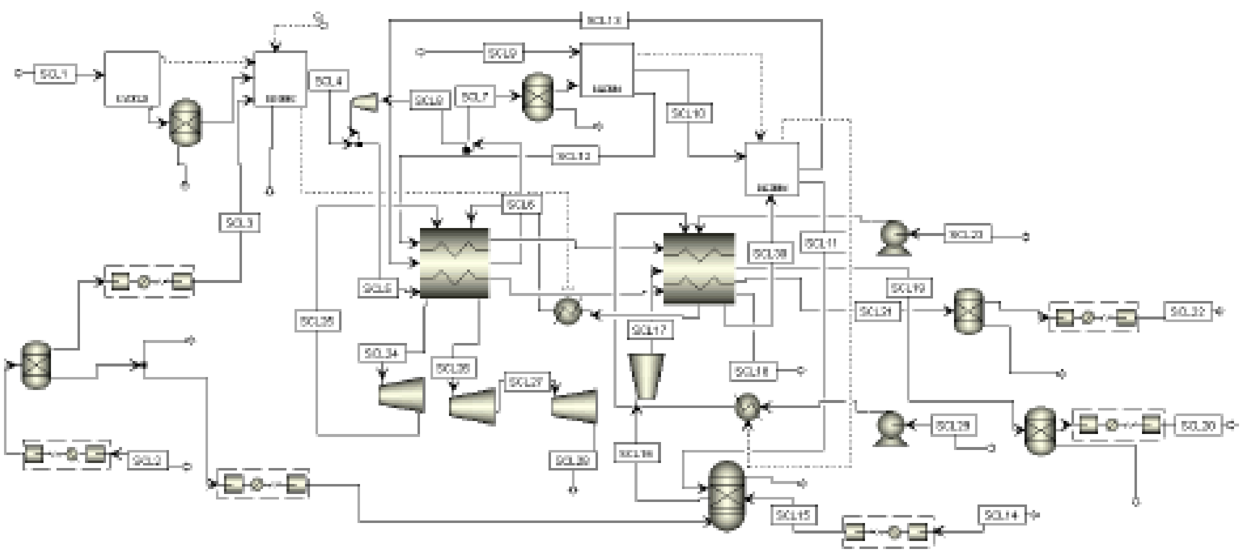
Traditional Coal to Hydrogen Process





Syngas Chemical Looping Process

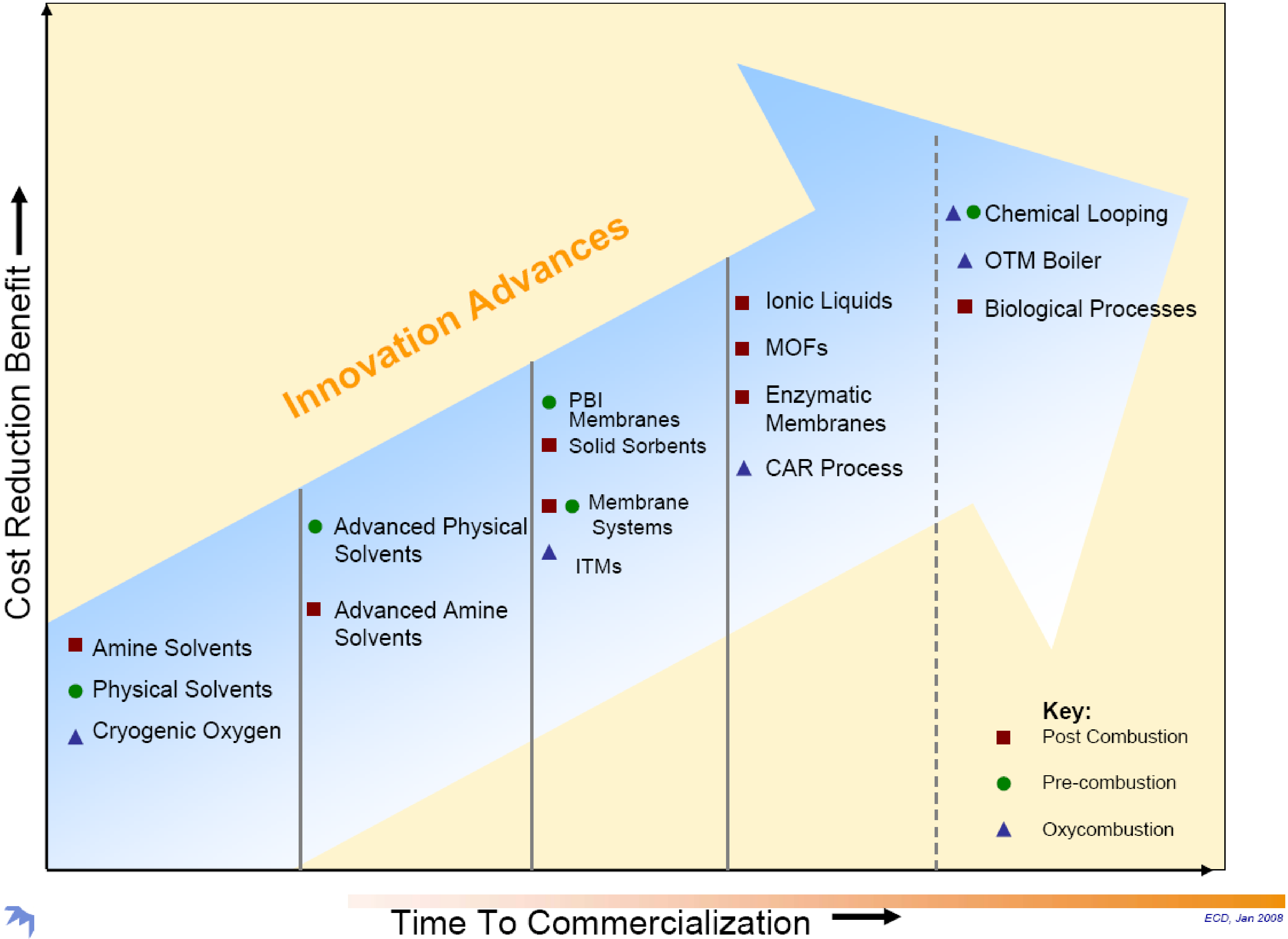




Comparison between SCL and Traditional Coal to Hydrogen/Electricity Process

	Conventional Max H_2	Conventional Co-Production	SCL
Coal feed (ton/hr)	132.9	132.9	132.9
Carbon Captured (%)	90	90	100
Hydrogen (ton/hr)	14.20	12.36	14.24
Net Power (MW)	0	38.9	66.2
Efficiency (%HHV)	**56.5**	**52.69**	**63.12**

SCL process can increase the efficiency of State-of-the-art coal to hydrogen process by 7 – 10%



Cost Reduction Benefit
Innovation Advances
Amine Solvents
Physical Solvents
Cryogenic Oxygen
Advanced Physical Solvents
Advanced Amine Solvents
PBI Membranes
Solid Sorbents
Membrane Systems
ITMs
Ionic Liquids
MOFs
Enzymatic Membranes
CAR Process
Chemical Looping
OTM Boiler
Biological Processes
Key:
Post Combustion
Pre-combustion
Oxycombustion
Time To Commercialization
ECD, Jan 2008

Process/Equipment Co-Simulation

Two scales of modeling for prediction

I Equipment Simulation in SCL System

- How equipments behave
- Fluent

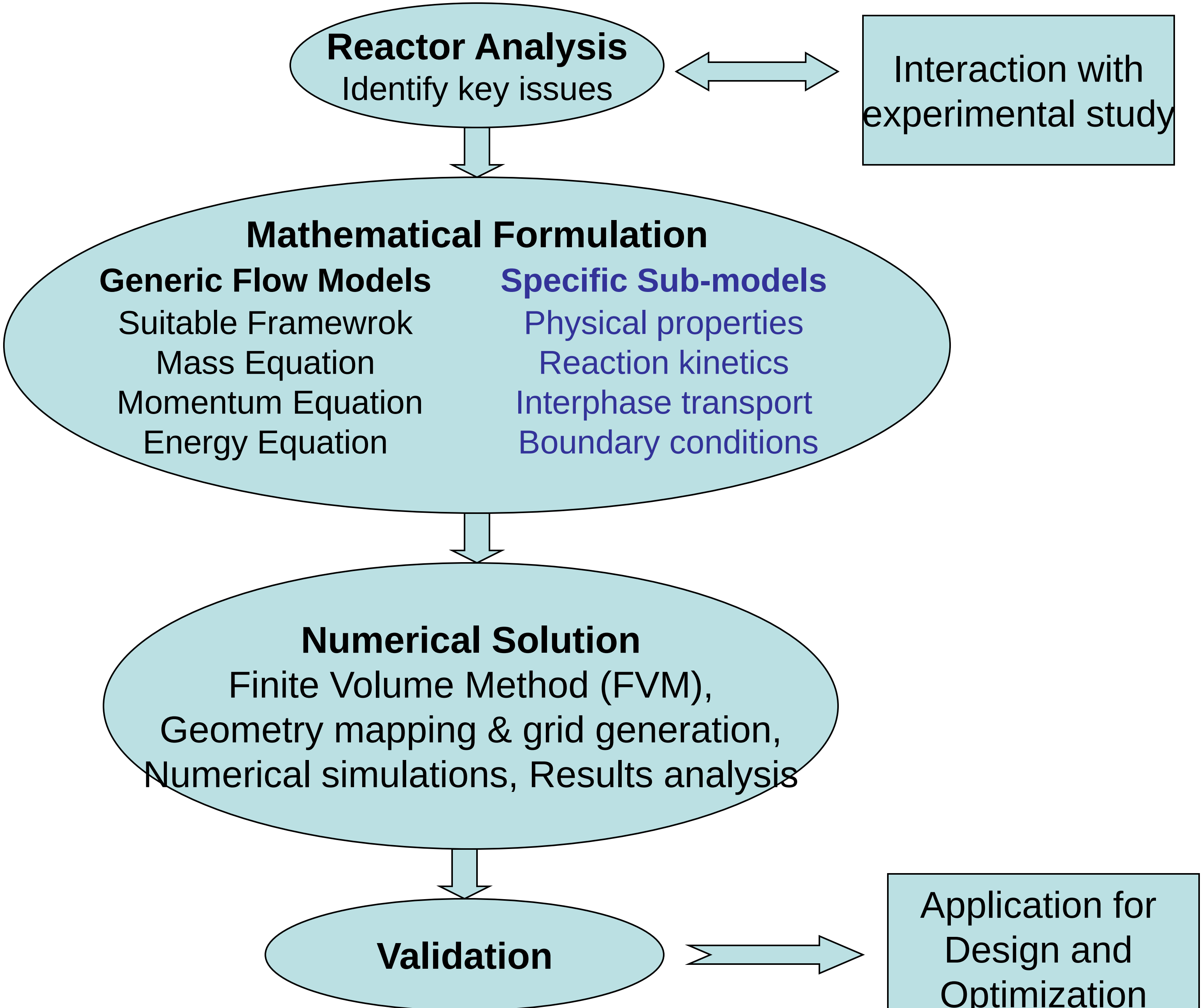
II Process Simulation on SCL Process

- How the whole process works
- Aspen Plus

Equipment vs. Plant Modeling

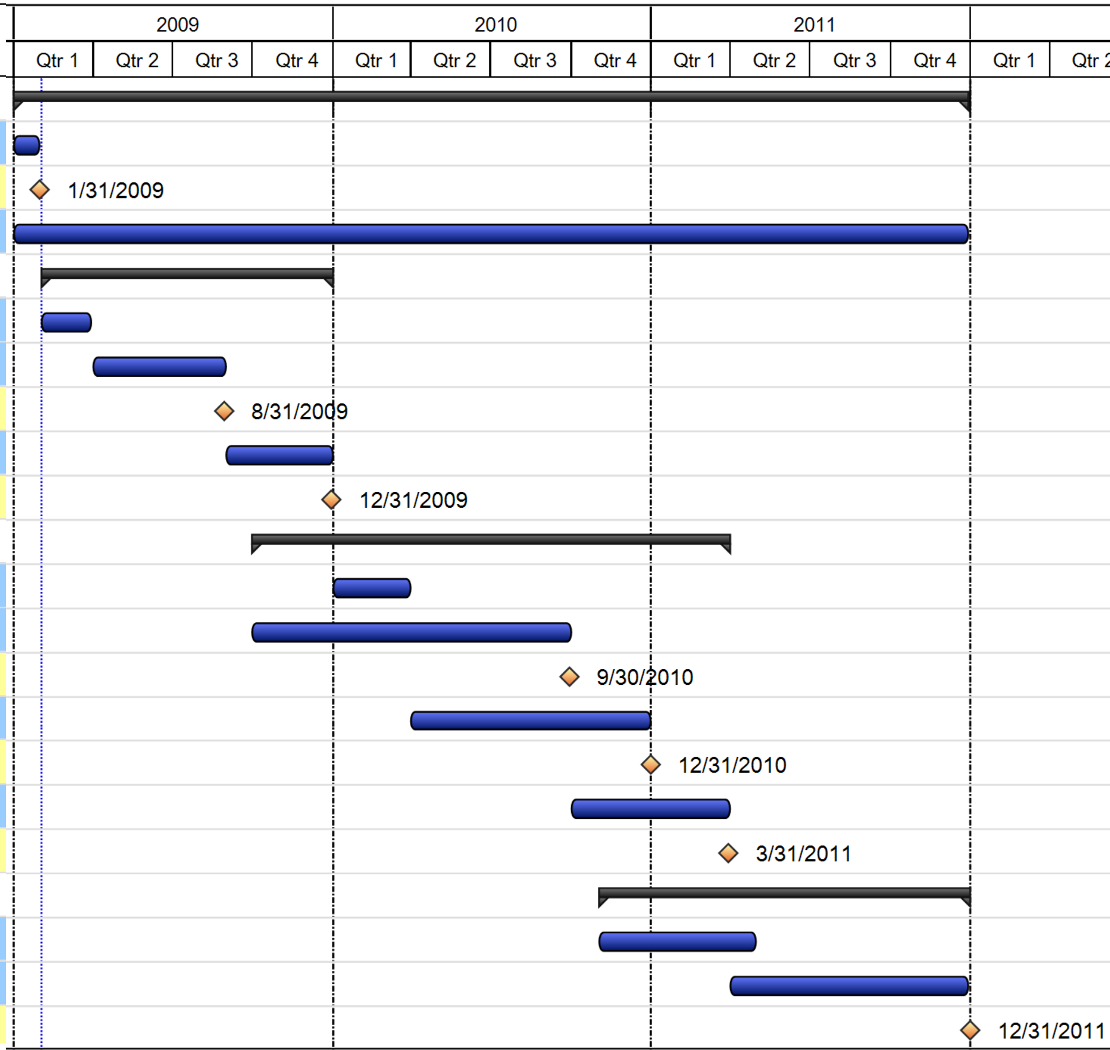
Software	**Fluent**	**Aspen Plus**
Scale	Equipment	Entire plant
Resolution	2D/3D	0D/1D
Balance	Distributed mass/heat/momentum balances	Overall mass/heat balances
Advantages	Many physical submodels	Extensive physical properties database
Use	Equipment optimization, flow field visualization	Process design, overall efficiency
Method	Computational Fluid Dynamics (CFD)	Steady-State Process Simulation

Equipment Simulation in Fluent



Overall Project Timeline

#	Name
1	**Task 1.0 – Project Management and Planning**
2	Subtask 1.1 Preparation of Project management Plan
3	Milestone 1. Submission of the revised of PMP and the kickoff meeting
4	Subtask 1.2 Project Management and Reporting
5	**Task 2.0 – Primary Thermodynamic Modeling**
6	Subtask 2.1 Fates of H2S, NOx and mercury
7	Subtask 2.2 SCL process for hydrogen production
8	Milestone 2. Performance Report for Hydrogen Production
9	Subtask 2.3 SCL process for electricity generation
10	Milestone 3. Performance Report for Electricity Generation
11	**Task 3.0 – Reactor Modeling**
12	Subtask 3.1 Physical Property Model
13	Subtask 3.2 Reaction Mechanisms
14	Milestone 4. Reaction Kinetic Modeling Report
15	Subtask 3.3 Reducer Modeling
16	Milestone 5. Reducer Modeling Report
17	Subtask 3.4 Combustor Modeling
18	Milestone 6. Combustor Modeling Report
19	**Task 4.0 – Advanced Process Modeling**
20	Subtask 4.1 Primary Integration
21	Subtask 4.2 APECS Analysis
22	Milestone 7. APECS analysis report



Conclusions

- The SCL process is an effective way to produce hydrogen from coal with CO_2 capture
- Thermodynamic analysis and equilibrium based reactor modeling prove the advantage of moving bed reactor application
- Experimental study validates the modeling work
- Process simulation shows the mass and energy management in the SCL process
- CFD modeling is in progress

Acknowledgement

- UCR, USDOE
- Ohio Coal Development Office (OCDO) and The Ohio Air Quality Development Authority (OAQDA)
- US Air Force

Thanks